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FORMATION MECHANISM AND ADHESIVE STRENGTH OF WHITE SINGLE-LAYER LOW-MELTING ENAMELS ON STEEL

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The formation mechanism of white single-layer glass enamel coating on steel surface in low-temperature firing is considered. The basic laws governing strong adhesion are identified. The effect of various methods of pre-treatment of steel before single-layer low-temperature enameling on the structure and composition of the transitional adhesive contact layer determining the adhesion strength of steel – enamel composite is demonstrated.

An efficient method for decreasing production costs and improving the quality parameters of enameled products is the use of single-layer enameling employing white vitreous coatings. Enameled parts of household equipment (gas stoves, electric stoves, water heaters) are steel facing sheets with substantial surface, whose firing temperature should not exceed 700 – 720°C, to prevent their warping. Therefore, the use of low-melting white single-layer vitreous coating is promising. The main factors that enable one to obtain a high-quality coating are the physicochemical processes in the contact metamorphosis zone of the steel-enamel system, as a consequence of which an intermediate adhesive layer is formed.

The white low-melting glass enamel coating synthesized in the $R_2O - Sl_2O_3 - B_2O_3 - SiO_2 - TiO_2 - P_2O_5$ system has a melting point of 1100 – 1200°C. The formation of coating on steel proceeds for 5 min at the temperature of 680 – 700°C. The absence of adhesive pigment oxides (CoO and NiO) in the enamel composition and a low formation temperature make it rather difficult to attain strong adhesion in steel-coating composite. In this case, one of the methods for ensuring adhesion is special treatment of the steel surface to intensify the chemical reactions arising under different kinds of steel treatment.

The studies revealed that a necessary, although insufficient condition for strong adhesion of single-layer low-temperature enamel implies mechanical treatment of the metal surface to produce a well-developed relief. This increases several times the surface area of the contact between the metal substrate and the glass enamel coating. In this case, the strength of the steel-enamel composite increases due to anchor adhesion. The data of strength tests of enameled samples using the gradual deformation method (Fig. 1) shows that the adhesion index is significantly higher in the case of using mechanical (shot-blast treatment) and chemical (deep etching) methods to increase the metal surface roughness than when traditional methods of treatment are employed (degreasing, etching, neutralization, and chemical nickeling). An adhesion index of 50% or less, which is provided by a predominantly mechanical method, is insufficient for enameled products. Therefore, another necessary condition for a strong composite is to provide the possibility for chemical reactions in the contact area. This leads to formation of adhesive phases and facilitates strong adhesion of enamel to steel.

As white glass enamel coating is formed on steel treated by various methods, adhesive phases are not formed in low-

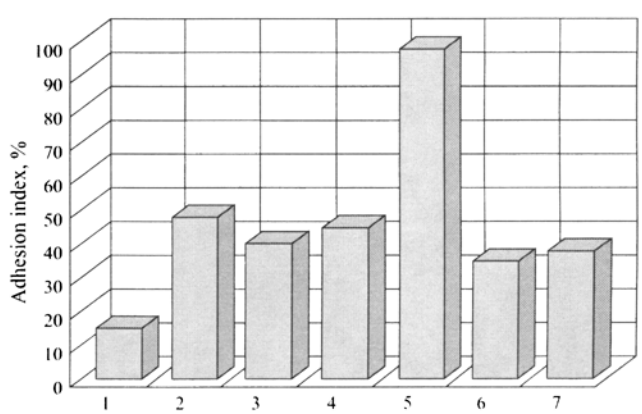

Fig. 1. Relationship of the adhesive strength of steel/white enamel composite on the method of metal treatment: *1*) traditional treatment and nickeling treatment; *2*) shot-blast treatment; *3*) shot-blast treatment and chemical nickeling; *4*) shot-blast treatment and thermal oxidation; *5*) shot-blast treatment, nickeling, and oxidation; *6*) deep etching; *7*) deep etching and nickeling.

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temperature firing (680 – 700°C). This is indicated by the low adhesion indexes of the steel-enamel composite and complete separation of coating together with the contact oxide layer from the steel surface when the sample is deformed. This is the result of the low firing temperature of the coating, as a consequence of which an oxide layer, which consists mostly of Fe_3O_4 and Fe_2O_3, is formed on the metal surface (the temperature of their formation is 200 – 400°C).

If adhesive oxides (CoO and NiO) are absent in a glass enamel coating, FeO can participate in electrochemical reactions in firing. Therefore, it is necessary to maintain the predominant presence of the wustite phase (FeO) in the oxide layer on the steel surface: it is advisable in the course of firing to create conditions favorable for the formation of an oxide layer of the optimum thickness consisting mostly of FeO. It is known that wustite is the most reactive component with respect to glass enamel silicate melt. Therefore, if FeO is present in firing, the formation of ferrous-silicate phases is thermodynamically the most probable. Magnetite and hematite are only capable of dissolving in an enamel melt modifying its properties, mostly in high-temperature firing. Moreover, ferrous oxides (FeO, Fe_3O_4, Fe_3O_3) have various orientation relations of crystal structures with respect to the main metal. Elastic stresses are accumulated in the exterior layers of the oxide film which consist mainly of Fe_3O_4 and Fe_2O_3, and the crystallographic orientation of these oxides significantly differs from the crystal structure of steel. Therefore, the bond between the steel surface and the wustite oxide phase is significantly stronger than its bond with the hematite and the magnetite phases.

Oxidation of the steel surface through the dry layer pores in the course of firing of the glass enamel coating proceeds intensely until the moment of enamel melt formation. As the result of steel oxidation at temperature above 700°C, the predominant phase in the oxide layer structure is wustite, and the remaining part is represented by Fe_3O_4 and Fe_2O_3.

Formation of synthesized glass enamel coating requires decreased firing temperatures, i.e., 680 – 700°C. Judging from the change in electric conductivity, the emergence of melt on the steel surface begins at 500 – 550°C. As a consequence, the access of oxygen to the metal is impeded, and metal oxidation is sharply decreased. Since the formation of wustite (FeO) is only possible at the temperature of 575°C or higher, the emerging oxide layer has insufficient thickness, and FeO is almost totally absent from its composition. Therefore, in order to intensify steel oxidation in the contact zone and provide for wustite formation, preliminary heat treatment of the steel surface at a temperature of 580°C and higher is required. For this purpose, isothermal treatment of the steel samples after undergoing shot-blast treatment were performed for 1 – 2 min.

It was found that thermal treatment is especially effective in steel oxidation after shot-blast treatment and chemical nickeling of steel (Fig. 1). This results in a steel-enamel composite with the highest adhesive strength. Nickel is deposited on the steel surface as a result of the reaction between nickel sulfate and iron, according to the reaction $Fe + NiSO_4 = Ni + FeSO_4$, during which a jump in the potential occurs and the following reaction takes place: $Fe^0 + Ni^{2+} = Ni^0 = Fe^{2+}$ ($\Delta G^0_{298\,K} < 0$). As a glass enamel coating is formed on the metal treated in the specified way, a nickel layer approximately 0.7 μm thick impedes the formation of Fe_3O_4 and Fe_2O_3 in the initial phase of firing.

Simultaneously with steel protection against excessive oxidation, nickel is oxidized to NiO and reacts with FeO at 500 – 680°C with the formation of a solid solution (Fe,Ni)O. Next, the contact area between the metal oxide layer and the enamel silicate melt reacts with $[SiO_4]^{4-}$ anions with the formation of $(Fe,Ni)_2SiO_4$, which is supported by petrographic and x-ray analysis data. Such crystalline phase is uniformly distributed over the transitional layer, which is a vitreous phase saturated with ferrous oxides. This provides for its strong adhesion both to steel and to the coating.

As the coating breaks off in the course of testing, a light brown adhesive layer is seen on the metal surface and on the enamel reverse side, which is evidence of the reaction which had taken place at the coating-steel interface during firing with emergence of the adhesive phase.

Thus, a strong composite of steel and white low-melting glass enamel coating can be produced using preliminary integrated treatment of the metal surface, including shot-blast treatment, chemical nickeling, and thermal oxidation. The above method for enameling steel large-size sheet parts is recommended for use in industry.